

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
26 February 2004 (26.02.2004)

PCT

(10) International Publication Number
WO 2004/016566 A1

(51) International Patent Classification⁷: C04B 14/00, C09C 1/04

(21) International Application Number:
PCT/US2003/025591

(22) International Filing Date: 14 August 2003 (14.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/219,540 15 August 2002 (15.08.2002) US

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant: J.M. HUBER CORPORATION [US/US];
333 Thornall Street, Edison, NJ 08837 (US).

(72) Inventors: CARTER, Richard, Douglas; 5261 Whitehouse Plantation Road, Macon, GA 31210 (US). ISHLEY, Joseph; 1324 Maplewood Drive, Macon, GA 31210 (US).

(74) Agents: NIEVES, Carlos et al.; J.M. Huber Corporation,
333 Thornall Street, Edison, NJ 08837 (US).

Declaration under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COATING COMPOSITION INCLUDING A PRECIPITATED CALCIUM CARBONATE AND A GROUND CALCIUM CARBONATE

(57) Abstract: A method for preparing a pigment composition is provided which produces a calcium carbonate pigment composition that imparts effective light-scattering, gloss, and opacity performance to paper. The pigment is useful in other materials as well, besides paper. The method consists essentially of the steps of providing a precipitated calcium carbonate having a median particle size, by weight, of less than about 1.6 micrometers; providing a ground calcium carbonate having a median particle size, by weight, of less than about 0.8 micrometers; and mixing the precipitated calcium carbonate with the ground calcium carbonate in a weight ratio of precipitated calcium carbonate to ground calcium carbonate of from about 3:2 to about 1:9 to form the pigment composition.

WO 2004/016566 A1

TITLE OF THE INVENTION

[0001] Coating Composition Including a Precipitated Calcium Carbonate and a Ground Calcium Carbonate

BACKGROUND OF THE INVENTION

5 [0002] Calcium carbonate is currently used as an additive in a wide variety of consumer products, particularly foods and paper. In food products, calcium carbonate not only supplies the body with an essential nutrient (calcium), but also serves as a hydrophobic conditioner to prevent caking in food powders

[0003] In paper products calcium carbonate is a pigment typically used as a filler or
10 coating material. While calcium carbonate is not suitable for use in some acid-based paper making processes, it is a desirable filler material because it is relatively inexpensive and imparts good light scattering efficiency to paper resulting in a brighter, more opaque paper, while also providing a high resistance to yellowing and aging. Ground calcium carbonate, which is formed by grinding calcium carbonate obtained from natural sources such as limestone or
15 chalk, can be found in both "standard", and "special" pigment filler grades. The "special" grades have a particularly narrow particle size distribution relative to standard GCC products. This narrow distribution results in a paper or coating structure having a pore size that is a more efficient scatterer of light and, thus these special ground calcium carbonate pigments impart enhanced optical properties, particularly brightness and opacity to paper products. However,
20 because these special ground calcium carbonate pigments are more expensive than conventional ground calcium carbonates, their use is limited to certain premium papers. Moreover, these special ground calcium carbonate pigments have frequently caused rheological and flow problems when incorporated in coating compositions for use in high speed paper coating equipment.

25 [0004] Thus, there is a need for alternatives to the special ground calcium carbonate materials that are less expensive and/or more rheologically suitable for use in high-speed coating equipment. In addition to "standard" ground calcium carbonates, another alternative to "special" GCC minerals is synthetic precipitated calcium carbonate ("PCC"), which can be cleanly and conveniently produced in a precipitation reaction by reacting Ca(OH)_2 ("milk of
30 lime") with carbon dioxide; water being generated as a by-product. The precipitation process produces a highly structured and/or narrow particle size distribution calcium carbonate pigment

that provides a high scattering performance when used in paper coating or filling applications. Calcium carbonate materials having characteristics such as high structure and narrow particle size distribution provide clear advantages when used in low solids applications, such as filler applications. However, calcium carbonate materials having these characteristics may also contribute to poor slurry rheology when used in high solids coating applications, and additionally such calcium carbonate materials can also create challenges in obtaining sufficient gloss performance on coated sheets. By modifying the precipitation reaction conditions the rheology and/or gloss can be improved, but typically only at the cost of lower scattering efficiency and a reduction in the economic practicality of the PCC coating pigments. Thus, for the vast majority of today's paper coating applications, the PCC coating pigment is a high cost alternative.

[0005] Given the forgoing there is a continuing need for calcium carbonate materials that are both cost-effective, and also impart effective light-scattering, gloss, and opacity performance to paper. For reasons of cost and convenience, such calcium carbonate materials would ideally be a blend of ground calcium carbonate and precipitated calcium carbonate. Preferably, these calcium carbonate blends would also not have the problems, such as low gloss and poor runnability, typically observed in other such blended compositions.

BRIEF SUMMARY OF THE INVENTION

[0006] The invention includes a method for preparing a pigment composition, consisting essentially of the steps of: providing a precipitated calcium carbonate having a median particle size, by weight, of less than about 1.6 micrometers; providing a ground calcium carbonate having a median particle size, by weight, of less than about 0.8 micrometers; and mixing the precipitated calcium carbonate with the ground calcium carbonate in a weight ratio of precipitated calcium carbonate to ground calcium carbonate of from about 3:2 to about 1:9 to form the pigment composition.

[0007] The invention also includes a pigment composition comprising a blend of ground calcium carbonate and precipitated calcium carbonate, wherein a plotted histogram of the particle size distribution curve of the pigment composition shows only a single peak.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0008] The foregoing summary, as well as the following detailed description of preferred embodiments of the invention, will be better understood when read in conjunction with the appended drawing. For the purpose of illustrating the invention, there is shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

10 [0009] Fig. 1 is a graph illustrating the particle size distribution of a pigment composition prepared according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0010] All parts, percentages and ratios used herein are expressed by weight unless otherwise specified. All documents cited herein are incorporated by reference.

15 [0011] The present invention relates to blends of "standard" ground calcium carbonate (i.e., ground calcium carbonate that has a conventional particle size distribution) and precipitated calcium carbonate pigments that when incorporated into a paper coating composition provide excellent light scattering, brightness, opacity and gloss performance. This improved light scattering efficiency is caused by the precipitated calcium carbonate pigment particles disturbing the standard ground calcium carbonate structure resulting in pores that are found in the optimum size range (e.g., between 0.18 μm and 0.22 μm). The precipitated calcium carbonate pigment particles are sufficiently small so that they do not impair the gloss performance.

25 [0012] The ground calcium carbonate included in the blends prepared according to the present invention is first mined and then ground to the appropriate particle size. The calcium carbonate may be mined from different, naturally occurring deposits of calcium carbonate ores such as chalk, limestone, or marble. Depending on the specific mineral, and its location, the calcium carbonate ores can be of different levels of purity and chemical composition. Chalk generally has the lowest impurity level, calcitic limestone the next lowest concentration of impurities, while white marble has the highest impurity concentration. The most common
30 impurities are magnesium carbonate and silica. The calcium carbonate is ground in a multi-step

process in which one or more grinding steps may alternate with other intermediate processing steps, such as comminution and flotation, dispersing and other appropriate processing steps. Grinding may occur using known grinding media (such as alumina or silica granules) or by the action of the calcium carbonate particles grinding each other ("autogenous" grinding). Wet grinding may be used if desired. Typically, the first step is a primary grinding step in which the calcium carbonate ore is reduced in particle size by autogenous grinding. Next a flotation step is used to remove non-carbonate impurities so that the resulting product is almost pure calcium carbonate. This flotation step is often followed by one or more grinding steps making use of grinding media. The process of preparing ground calcium carbonate is well-known to those of ordinary skill in the art and is described in greater detail in U.S. Patent No. 6,003,795.

[0013] The grinding of the calcium carbonate continues until such time that the ground calcium carbonate has a particle size that is characteristic of the Grade V type ("Superfine") according to the specification of ASTM Standard D1199-86. Specifically, the ground calcium carbonate will have a median particle size, by weight, of less than about 0.8 micrometers; and about 90 wt% of the ground calcium carbonate has a particle size of less than about 2 μm ; and about 65 wt% of the ground calcium carbonate will a particle size of less than about 1 μm .

[0014] Suitable ground calcium carbonates are manufactured by the J.M. Huber Corporation and are sold in different grades under the trade name Hubercarb®. Other suitable ground calcium carbonates are manufactured by Omya GmbH (Cologne, Germany) under the trade names Covercarb™ (which is "special" ground calcium carbonate having a particular narrow particle size distribution) and Hydrocarb™ (which is "standard" ground calcium carbonate, having a particularly narrow particle size distribution).

[0015] Precipitated calcium carbonate is obtained by exposing calcium hydroxide (i.e., milk of lime or slaked lime) to a carbonation reaction. This may be done by injecting carbon dioxide gas into a reaction vessel containing aqueous calcium hydroxide slurry. When prepared in such precipitation reactions, the calcium carbonate will be in either the rhombohedral or scalenohedral crystal habit. After being prepared in this manner, the precipitated calcium carbonate will have a median particle size, by weight, of less than about 1.6 micrometers, and about 98 wt% of the precipitated calcium carbonate has a particle size of less than about 5 μm ; and about 21 wt% of the precipitated calcium carbonate has a particle size of less than about 1 μm .

[0016] Methods and techniques for preparing these precipitated calcium carbonates are discussed in greater detail in U.S. Patent No. 4,888,160.

[0017] After being manufacture as described above, the precipitated calcium carbonate and ground calcium carbonate are blended together, preferably at a ratio of precipitate calcium carbonate to ground calcium carbonate of about 3:2 to about 1:9.

[0018] In a first step of this blending process, a slurry of the ground calcium carbonate is prepared in a mixer. The slurry should contain a concentration of ground calcium carbonate in the range of 72 wt% to 78 wt%. Next, an amount of dispersant (such as sodium polyacrylate) in the range of 0.3 wt% to 0.75 wt% (based on the dry weight of the precipitated calcium carbonate) should be added to the ground calcium carbonate slurry. The precipitated calcium carbonate is then added to the slurry of ground calcium carbonate, with the amount of precipitated calcium carbonate and ground calcium carbonate being present within the aforementioned desired weight ratios mentioned above. This mixing continues for at least five to ten minutes at a slow speed (and/or at low shear) to produce a substantially homogeneous slurry. This homogeneous slurry is then transferred to a high shear mixer (or mixed at a higher speed/shear) and mixed for at least ten to fifteen minutes and this sheared slurry may then be incorporated into a paper coating. Suitable mixing equipment includes a cowels mixer, or any suitable open impeller flat blade mixer. Other suitable mixing equipment includes a closed impeller device, such as a kady mill. all of this equipment preferably has a continuous speed control.)

[0019] Alternatively, the above method may be modified slightly so that the dispersant is added directly to the precipitated calcium carbonate to create a premix of dispersant and precipitated calcium carbonate. (The dispersant is added in the same weight proportions mentioned above.) The premix is then mixed in a low speed mixer until it is substantially homogenous. Then the premix is combined with the slurry of ground calcium carbonate (in the same weight proportions mentioned above) and mixed in a high shear mixer (such as a Cowels mixer) for at least ten to fifteen minutes. After being prepared in the above manner, the particle size (the equivalent spherical diameter or "esd") was measured by a Sedigraph particle size analyzer (Model 5100), manufactured by Micrometrics Instrument Corp., Norcross, Ga.). This is a sedimentation type instrument, which uses Stokes Law in determining the equivalent

spherical particle diameters. The use of such equipment to determine particle size is well within the capabilities of a person of ordinary skill in the art.

[0020] By taking several esd measurements, a particle size distribution curve of the PCC materials prepared according to the present invention (which is a blend of the precipitated calcium carbonate and ground calcium carbonate) was constructed, which is shown in Fig. 1. As can be seen, the pigment composition prepared according to the present invention has a particle size distribution curve, which when represented as a graph of percentage by weight of particles having a particle esd of a specific size(y-axis) versus particle esd (x-axis), has only a single peak, with no "shoulder" being present.

10 [0021] In practice, Fig. 1 was constructed by plotting the particle esd along the x-axis in esd size ranges. However, Fig. 1 is good approximation of a graph in which the esd is plotted as a continuous variable. This graph was constructed (as discussed above) by measuring a standard particle size distribution curve (weight percentage of particles having less than a specified esd) for a PCC blend and then extracting data for percentage of particles in each of the particle size ranges shown in the curve. The method of preparing the PCC material that is analyzed in the curve, is discussed below in the examples.

15 [0022] As discussed above, the precipitated calcium carbonate/ground calcium carbonate pigment blends prepared according to the present invention may be incorporated into a coating composition and applied to the paper where they have been demonstrated to provide lighter scattering efficiency and gloss performance comparable to that of special ground calcium carbonate materials. The calcium carbonate prepared according to the present invention is typically used in coating compositions for manufacturing paper from wood pulp. Sources of wood pulp may include any fibrous raw materials including hardwood, softwood, nonwood, straw, bamboo, hemp or recycled paper, board, or mixtures different fibrous raw materials. Besides the fibrous raw materials, and a coating composition, the present papers may also include cationic polymers (to impart dry strength to the paper); dyes (to produce colored paper); other coating materials and minerals besides calcium carbonate. The present papers may also include fillers such as kaolin or other clays, silica, synthetic silicates; calcium stearate (lubricant); plastic pigment; and other paper additives known to those of ordinary skill in the art.

Examples

[0023] Blends of ground calcium carbonate and precipitated calcium carbonate were prepared according to the present invention. The precipitated calcium carbonate was prepared in both the scalenohedral and rhombohedral forms. The scalenohedral precipitated calcium carbonate was prepared in the following fashion. The scalenohedral was formed by reacting 60 kg of French quick lime supplied by Carrieres de Boulonnais SA (grade BK0035) with 240 liters of water (pre-heated to 60°C) for ½ hour. 30 grams of Sodium Thiosulfate was added. After reaction the milk of lime was diluted to 14.3% solids (105°C) and screened on 200 µm. At this point, the Brookfield viscosity of the milk of lime was 70 cps (using a number 2 spindle at 100 rpm and 23°C) and the specific surface area (BET) was 23.3 m²/g. Then, the screened milk of lime was transferred to a 600 liter stirred tank reactor agitated at 250 rpm. The temperature was adjusted to 40°C and 105 g sucrose was added to the reactor, whereupon a 20% CO₂-air mixture was added at a rate of 90 m³/hour. Carbonization was continued for 2 hours until essentially all the Ca(OH)₂ had reacted to CaCO₃ as determined by conductivity measurements. The slurry was then screened at 45µm, and had the following properties after completion of the reaction. The properties of the slurry were measured as follows:

Table I

Property	Value
Median Particle Size (Sedigraph 5100)	1.78 µm
Specific Surface area (BET)	11.1 m ² /g
Solids (105°C)	18.3 %
ISO-brightness R457 (Tappi 534)	96.7
Brookfield viscosity	32 cps (number 2 spindle; measured at 100 rpm; 23°C)
PH	8.5

[0024] These data are indicative of a fine, aggregated scalenohedral PCC. The slurry was then dewatered into crumbles on a lab-scale Larox PF01 filter press. After which the solids were 57%. The scalenohedral precipitated calcium carbonate had the particle size distribution given in table II, below:

Table II

Summary of Particle size (esd) distribution for
scalenohedral-shaped, precipitated calcium carbonate

Particle size range	Wt%
> 10 μm	0.6%
10 μm – 5 μm	0.5%
5 μm – 2 μm	33.2%
1 μm – 2 μm	45.1%
0.5 μm – 1 μm	13.7%
0.2 μm – 0.5 μm	5.7%
< 0.2 μm	1.2%

5 [0025] The rhombohedral precipitated calcium carbonate was prepared in the following fashion. The rhombohedral precipitated calcium carbonate was prepared as follows. Three gallons of a calcium hydroxide aqueous slurry containing 17-20% solids was provided in a five gallon reactor vessel. The reactor contents were agitated at approximately 700-800 rpm using a 3 inch diameter turbine. Carbon dioxide was injected at a turbulent area comprising a bend in
10 the recycle piping system, downstream of which bend an in-line static mixer was provided. The initial pH of the aqueous slurry was approximately 11.5 to 12.0. The carbon dioxide was injected until the pH dropped to 9.0, at which time the carbon dioxide flow was stopped, and the batch was allowed to recycle and agitate for a period of ten to fifteen minutes. During this digestion period, the pH rose to about 10.5 to 11 as a result of the calcium carbonate
15 precipitates forming at the surface of the calcium hydroxide particles and then flaking off to expose new calcium hydroxide surfaces. The carbon dioxide injection was then resumed until the pH of the mixture was adjusted back to 9.0. The resultant precipitated calcium carbonate product had virtually no unreacted calcium hydroxide present.

[0026] The PCC in rhombohedral form had the particle size distribution given in table
20 III, below:

Table III

Summary of particle size (esd) distribution for
rhombohedral-shaped, precipitated calcium carbonate

Particle size range	Wt%
> 10 μm	0.7
10 μm – 5 μm	0.3
5 μm – 2 μm	24.3
1 μm – 2 μm	37.5
0.5 μm – 1 μm	31.2
0.2 μm – 0.5 μm	5.9
< 0.2 μm	0.1

- 5 [0027] The ground calcium carbonate used in the blend was Hydrocarb® 90 available from Omya GmbH. The mixture of ground calcium carbonate and precipitated calcium carbonate had the particle size distribution given in table IV, below:

Table IV

Summary of Particle size (esd)
distribution for Ground Calcium Carbonate

Particle size range	Wt%
> 10 μm	0.3%
10 μm – 5 μm	0.2%
5 μm – 2 μm	8.3%
1 μm – 2 μm	26.2%
0.5 μm – 1 μm	27.6%
0.2 μm – 0.5 μm	20.9%
< 0.2 μm	16.5%

- 10
- 15 [0028] The precipitated calcium carbonate, characterized by the particle size distribution given in tables II-III, and ground calcium carbonate, characterized by the particle size distribution given in table IV, were then blended to form an inventive blend of calcium carbonate. This inventive blend calcium carbonate had the particle size distribution given in table V, below:

Table V

Summary of Particle size
distribution for inventive blend of calcium carbonate

Particle size range	Wt%
> 10 μm	0.2%
10 μm – 5 μm	1.1%
5 μm – 2 μm	10.3%
1 μm – 2 μm	26.0%
0.5 μm – 1 μm	32.3%
0.2 μm – 0.5 μm	25.4%
< 0.2 μm	4.7%

5

[0029] The particle size distribution of Table IV is plotted in Figure 1. As can be seen there is only a single peak in the distribution.

[0030] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

15

CLAIMS

We claim:

1. A method for preparing a pigment composition, consisting essentially of
5 the steps of:

a) providing a precipitated calcium carbonate having a median
particle size, by weight, of less than about 1.6 micrometers;

10 b) providing a ground calcium carbonate having a median particle
size, by weight, of less than about 0.8 micrometers; and

c) mixing the precipitated calcium carbonate with the ground calcium
carbonate in a weight ratio of precipitated calcium carbonate to ground calcium carbonate of
15 from about 3:2 to about 1:9 to form the pigment composition.

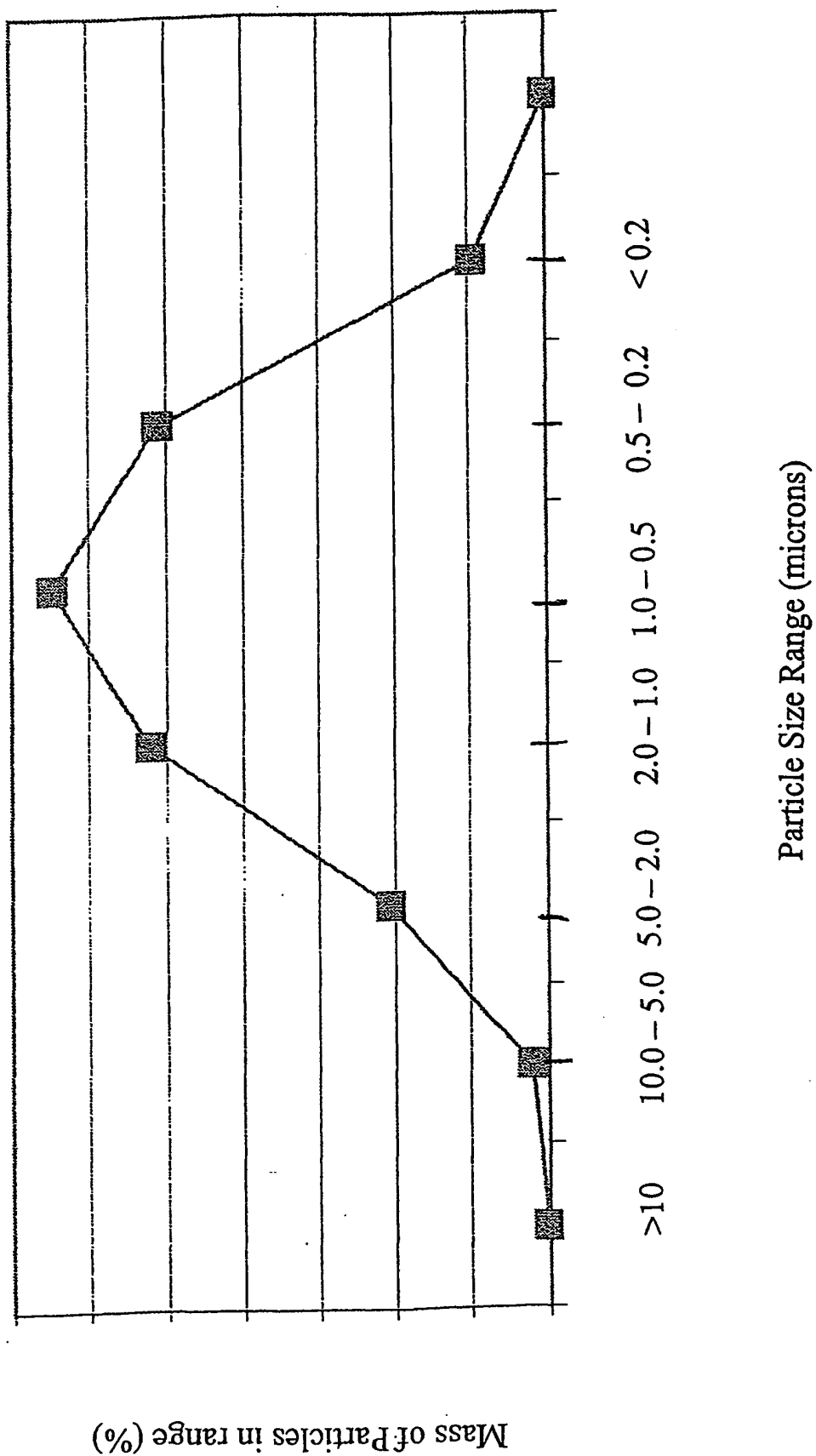
2. The method according to claim 1, wherein the precipitated calcium
carbonate having a median particle size of less than about 1.6 micrometers, and wherein about
98 wt% of the precipitated calcium carbonate has a particle size of less than about 5 μm ; and
20 about 21 wt% of the precipitated calcium carbonate has a particle size of less than about 1 μm .

3. A coating composition comprising the pigment composition prepared
according to the method of claim 1, wherein the coating composition has a pore size of about
0.18 μm to about 0.22 μm .

25 4. The method according to claim 1, wherein a plotted histogram of the
particle size distribution curve of the pigment composition in step (c) has that has only a single
peak.

5. A pigment composition comprising a blend of ground calcium carbonate
30 and precipitated calcium carbonate, wherein a plotted histogram of the particle size distribution
curve of the pigment composition shows only a single peak.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/25591

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C04B 14/00; C09C 1/04

US CL : 106/424, 444, 463, 449

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/424, 444, 463, 449

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

US PAT; US-PGPUB; EPO; JPO; DERWENT, (precipitat (calcium carbonate mix ground calcium carbonate) ratio weight percent size particle method process histogram pigment median natural blend)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,879,442 A (NISHIGUCHI et al.) 09 March 1999, see entire document.	1-2
X	US 4,026,762 A (BAUMAN, H et al.) 31 May 1977, see entire document.	1-2, 4-5

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

09 October 2003 (09.10.2003)

Date of mailing of the international search report

27 OCT 2003

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. 703-305-3230

Authorized officer

Marian Knode

Telephone No. 703-308-0661

Marian Knode